Coherent Mechanism of Robust Population Inversion

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A coherent mechanism of robust population inversion in atomic and molecular systems by a chirped field is presented. It is demonstrated that a field of sufficiently high chirp rate imposes a certain relative phase between a ground and excited state wavefunction of a two-level system. The value of the relative phase angle is thus restricted to be negative and close to 0 or $-\pi$ for positive and negative chirp, respectively. This explains the unidirectionality of the population transfer from the ground to the excited state. In a molecular system composed of a ground and excited potential energy surface the symmetry between the action of a pulse with a large positive and negative chirp is broken. The same framwork of the coherent mechanism can explain the symmetry breaking and the population inversion due to a positive chirped field.

Radiation induced transfer, of ground state population, to a designated excited state is an extremely useful quantum manipulation. Such a manipulation sets the stage for subsequent clean experiments which are free from disturbances from ground state population. In coherent control as well as in quantum computing a complete population transfer can be used to prepare an almost pure initial state which is a prerequisite for many manipulations.

The direct approach to population inversion by applying a π pulse is plagued by the inability to precisely control the intensity and time duration of the excitation pulse. Moreover inhomogeneity in the sample, in particular the orientation of the transition dipoles related to the impinging field further hinder the direct approach. For a two-level-system (TLS) the solution to the inversion problem is known as adiabatic following[1–3]. Using a sufficiently chirped field so that the change in instantaneous frequency is small relative to the Rabi frequency, adiabatic conditions prevail resulting in a unidirectional population transfer.

For a molecular system composed of two potential surfaces (TPS) the problem of robust complete population transfer from the ground electronic state to the excited one becomes more difficult. Cao, Bardeen and Wilson[4,5] suggested a population inversion scheme also based on a chirped excitation pulse. Their explanation was given in the form of a wavepacket picture. A chirp leads to prolongation of the pulse duration while conserving the total spectral band-width. In the case of linear chirp, a new, instantaneous band-width can be identified as the reciprocal value of the total pulse duration. Population transfer between two molecular potentials then has two aspects. The total band-width of the pulse addresses both potentials at a certain range of the molecular internuclear distance where the range of available Bohr frequencies corresponds to the pulse spectrum. However the population transfer itself takes place through narrower coupling window defined by the instantaneous bandwidth. In the case of positive chirp, the ground state population is sequentially promoted to the excited state through the instantaneous window which moves from lower to higher interpotential energy difference. However, the excited state wavepacket moves in the opposite direction due to the potential gradient. Thus a new portion of the wavepacket, just being transferred, does not interfere with the old one preventing the stimulated emission

from happening. The result is the population inversion between two molecular electronic Born-Oppenheimer potentials.

In the present letter we present a unified viewpoint based on a simple coherent control analysis which can explain the mechanism of robust complete population transfer in both the two-level system (TLS) as well as for the two potential surface (TPS) scenario. The basic idea is to employ a control local in time which monotonically directs the system to its final objective.

A robust manipulation is obtained if a unidirectional approach toward the target of control is maintained. In the present case we want to control the total change in population $\frac{dN_g}{dt}$. Where N_g is either the ground state population in the TLS or the expectation of the projection on the ground electronic surface i.e. $N_g = \langle \hat{\mathbf{P}}_\mathbf{g} \rangle = \int |\psi_g(r)|^2 dr$. In both cases the Heisenberg equation of motion for the change of the ground state population induced by an electromagnetic field becomes[6,7]:

$$\frac{dN_g}{dt} = \frac{2}{\hbar} |\langle \psi_g | \hat{\mu} | \psi_e \rangle| |E(t)| sin(\phi_\mu + \phi_E) \tag{0.1}$$

where $\langle \psi_g | \hat{\mu} | \psi_e \rangle$ is the transition dipole moment, E(t) is the electromagnetic field and ϕ_μ and ϕ_E are phase angles of the transition dipole and the field, respectively. ψ_i, i=g,e is a ground and excited state wavefunction, respectively.

Applying Eq. (0.1) to the unidirectional population transfer $\psi_g \rightarrow \psi_e$ implies $\frac{dN_g}{dt} \leq 0$, which is controlled by the sum of phase angles ϕ_μ and ϕ_E. The phase of transition dipole $\langle \psi_g | \hat{\mu} | \psi_e \rangle$ is assembled during the excitation process and is therefore a function of the history of the amplitude and phase of the excitation field. If initially all the population resides on the ground state its initial phase has no relevance since it does not alter the phase of the transition dipole.

A chirped electromagnetic field of Gaussian envelope in frequency representation has the following form[4]

$$\tilde{E}(\omega) = \tilde{E}(\omega_0) \exp[-\frac{(\omega - \omega_0)^2}{2\Gamma^2} - i\chi' \frac{(\omega - \omega_0)^2}{2}] \quad , \tag{0.2}$$

where ω_0 is the transform-limited carrier frequency of the field, Γ is the spectral bandwidth of the pulse and χ' is the chirp rate in energy representation given by $dt/d\omega$. The chirp rate term causes a phase shift of each spectral component of the field proportional to its 'distance' from the carrier frequency. The field in time representation is given by its Fourier transform

$$E(t) = E_0 exp[-\frac{t^2}{2\tau^2} - i\omega_0 t - i\chi\frac{t^2}{2} + i\phi_E] \quad , \tag{0.3}$$

where χ is the linear chirp rate in the time representation $d\omega/dt$. Chirp results in prolongation of the pulse in time domain reducing local field intensity to conserve the total pulse energy $\tau^2 = 1/\Gamma^2 + \Gamma^2\chi'^2$. The chirp rate in time and frequency representations are then related by the formula $\chi = \chi'.\Gamma^2/\tau^2$.

Without loosing generality ϕ_E can be set to zero because a constant phase of the field maps onto the phase of the transition dipole moment. In this case the direction of the population transfer will be determined by the induced instantaneous phase of the transition dipole $\langle\psi_g|\hat{\mu}|\psi_e\rangle = |\langle\psi_g|\hat{\mu}|\psi_e\rangle|e^{i\phi_\mu}$. A phase angel $-\pi < \phi_\mu < 0$ throughout the process will guarantee a monotonic and robust population transfer.

To verify this insight on the mechanism, a numerical scheme to solve the time dependent Schödinger equation (TDSE) was employed for both the TLS and the TPS. An initial state is propagated in time using a Chebychev polynomial expansion of the evolution operator[8]. The propagation was realized in discrete steps with a time increment shorter by two-orders of magnitude than the pulse duration. For a TPS, we used the Fourier grid representation of the wavefunction[9] and the quantum operators. Typical computation parameters, summarized in Tab. I, were chosen by the criteria of a correct representation of the wavepacket in coordinate as well as in momentum spaces.

TABLE I. The typical values of the propagation parameters. The grid parameters are related only to a TPS.

Parameters	Typical value	Units
Time step	$4\pi/10$	a.u.
Number of time steps	200	
Pulse duration	$\sqrt{\pi/2}$	a.u.
Typical maximal Rabi frequency	1	a.u.
Width of the initial wavepacket	0.1	a.u.
Initial position of the wavepacket	0	a.u.
Grid spacing	0.05	a.u.
Number of grid points	256	

The reference TLS case is obtained by an on-resonant transform-limited Gaussian pulse, with integrated intensity which causes a complete 2π cycling from the ground state to the excited state and back. The top panel of Fig. 1 shows the total population on the ground state N_g as well as its time derivative $\frac{dN_g}{dt}$, both obtained independently from quantum wavefunctions propagated in time. The phase or the imaginary part the transition dipole moment gains first negative values making $dN_g/dt < 0$. Once all the population is transfered to the excited state, the imaginary part of the transition dipole moment changes sign and redirect the population flow back to the ground state.

The lower panels show the same process upon increasing the chirp rate. It is evident that the symmetry between excitation and deexcitation is broken leading eventually with sufficient chirp rate, to a monotonic population transfer. The imaginary part of the transition dipole moment is restricted to negative values in that case.

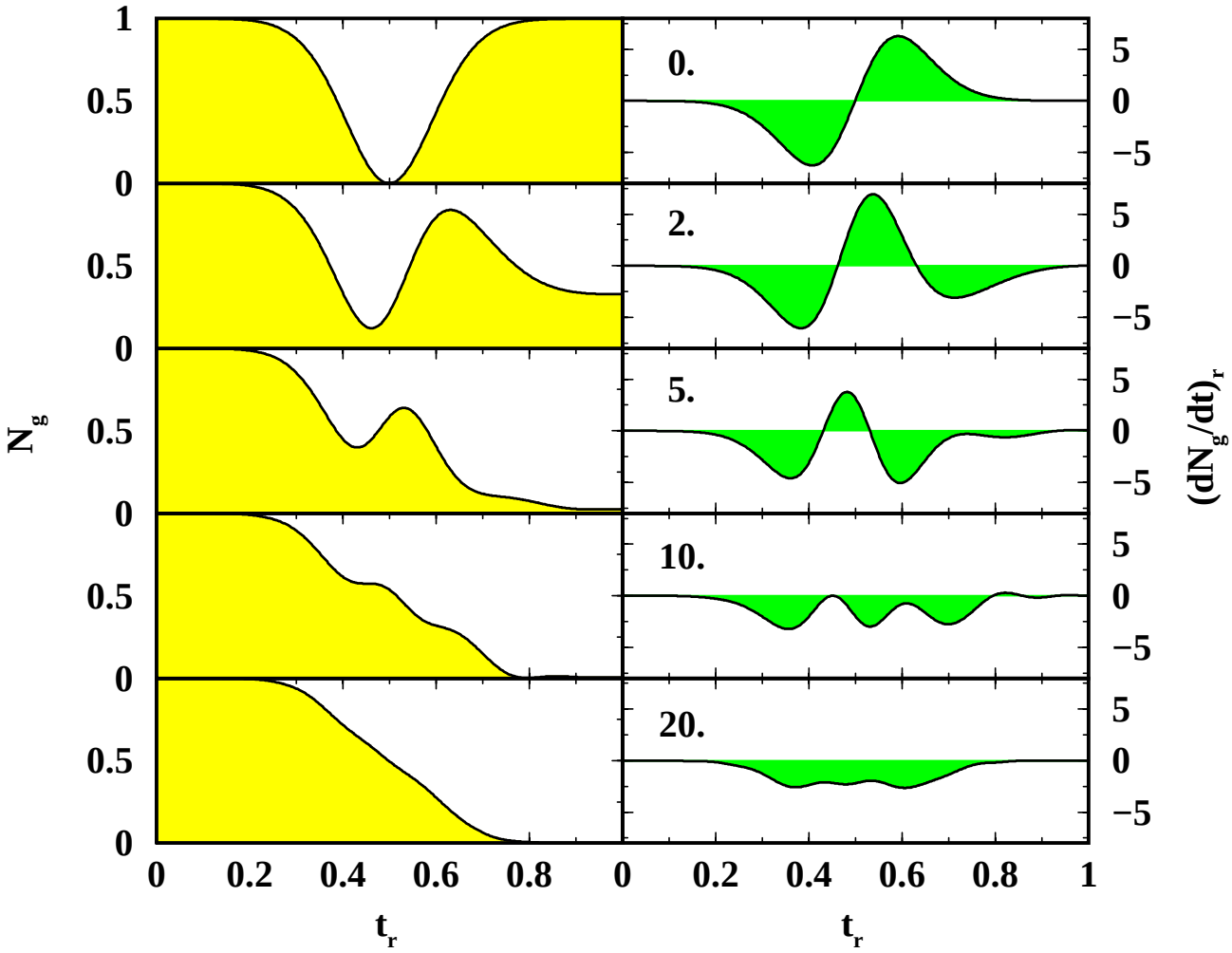

FIG. 1. The evolution of the ground state population $N_g(t)$ (left) and the imaginary part of the transition dipole moment multiplied by the field amplitude (right). The normalized time is defined as $t_r = t/(6\tau_{\chi'=0}.f)$ and $(dN_g/dt)_r = (6\tau_{\chi'=0}.f)dN_g/dt$ is the rate of change in the normalized time units. $\tau_{\chi'=0}$ is the pulse duration for a transform-limited pulse ($\chi' = 0$) and f is the ratio of pulse duration between the chirped and unchirped cases. The numbers indicate the value of the chirp rate.

Fig. 2 displays the transition dipole trajectories during the excitation process. For the on-resonant transform-limited pulse, the trajectory lies on the imaginary axis and the corresponding relative phase angle switches between $-\pi/2$ and $\pi/2$. With increasing chirp rate the trajectories also obtain a real component positive for the positive chirp and *vice*

versa. For the chirped field case more time is spent in the negative imaginary part of the complex plane. With sufficient chirp the whole trajectory is maintained in the negative quadrants. The perfect symmetry of the trajectories with respect to pulses with positive and negative chirp is obvious for this TLS case.

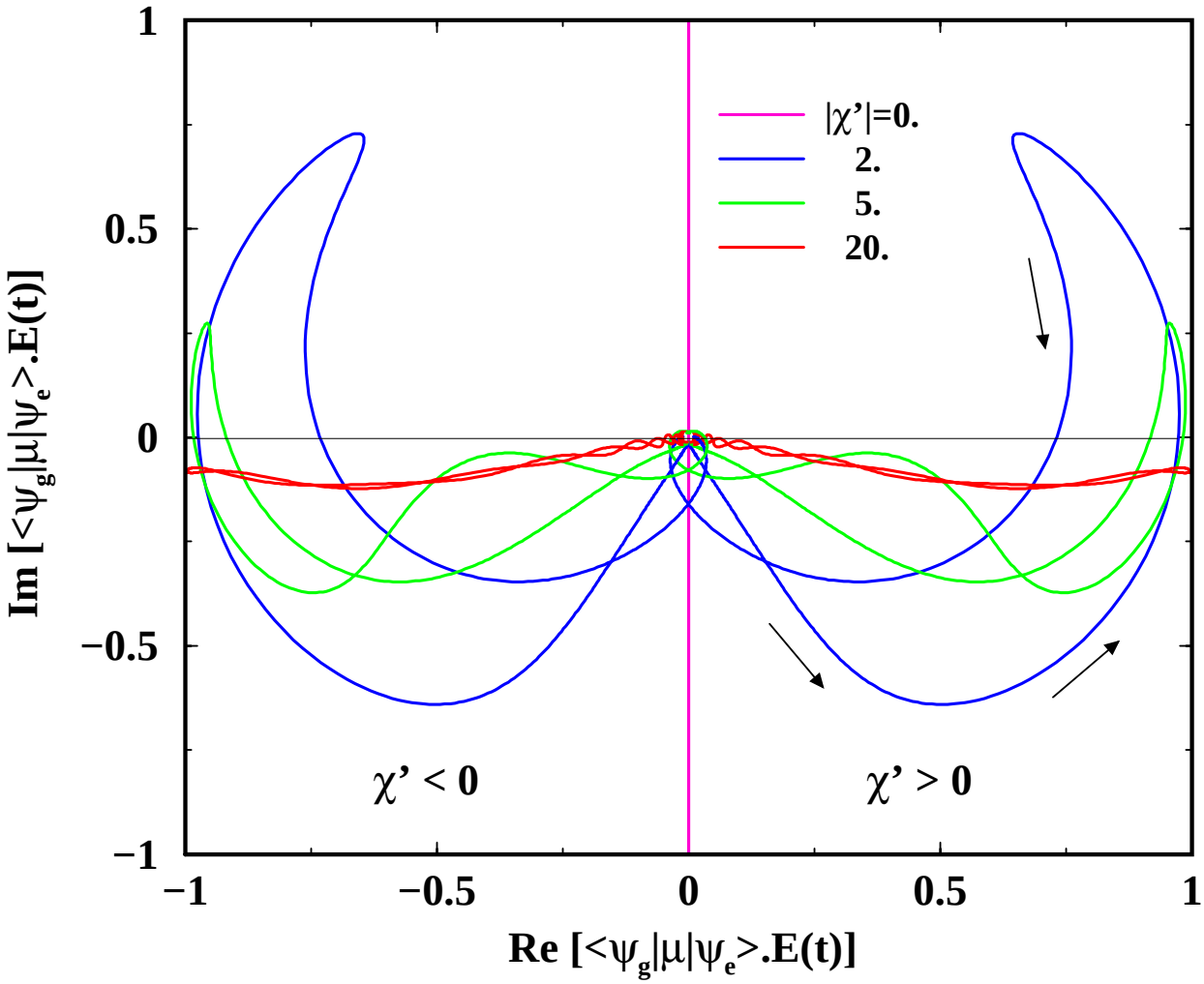

FIG. 2. Trajectories of the transition dipole moment, renormalized by its maximal amplitude, for excitation by the transform limited (on the imaginary axis) and chirped pulsed field of positive and negative chirp rates.

Chirped field excitation in a molecular systems is more involved due to the inherent dynamics of nuclear wavepackets on the ground and excited electronic potentials. A two-potential model is studied consisting of a flat ground state and a linearly decreasing excited

state potential. The field is assumed to be sufficiently broad band to address all the initial nuclear configurations on the ground electronic state. The intensity of the field is sufficient to transfer all the population.

Positive chirp results in complete population inversion. The instantaneous coupling window given by the instantaneous frequency of the chirped field moves in the direction from lower to higher Bohr frequency of the system. The excited wavepacket moves in the opposite direction due to the excited potential gradient[4,5]. The evolution of the imaginary part of the transition dipole is restricted to negative values locally in the instantaneous coupling window and thus the population transfer is unidirectional from the ground electronic potential.

Negative chirp leads to a different result. The coupling window now moves in the same direction as the excited state population. Due to this evolution the excited wavepacket gains an extra phase which breaks the subtle phase relations between the nuclear populations on the electronic potentials coupled by the field. The corresponding evolution of the imaginary part of the transition dipole moment is thus not restricted to negative values and the population transfer is not unidirectional as can be seen in Fig. 3.

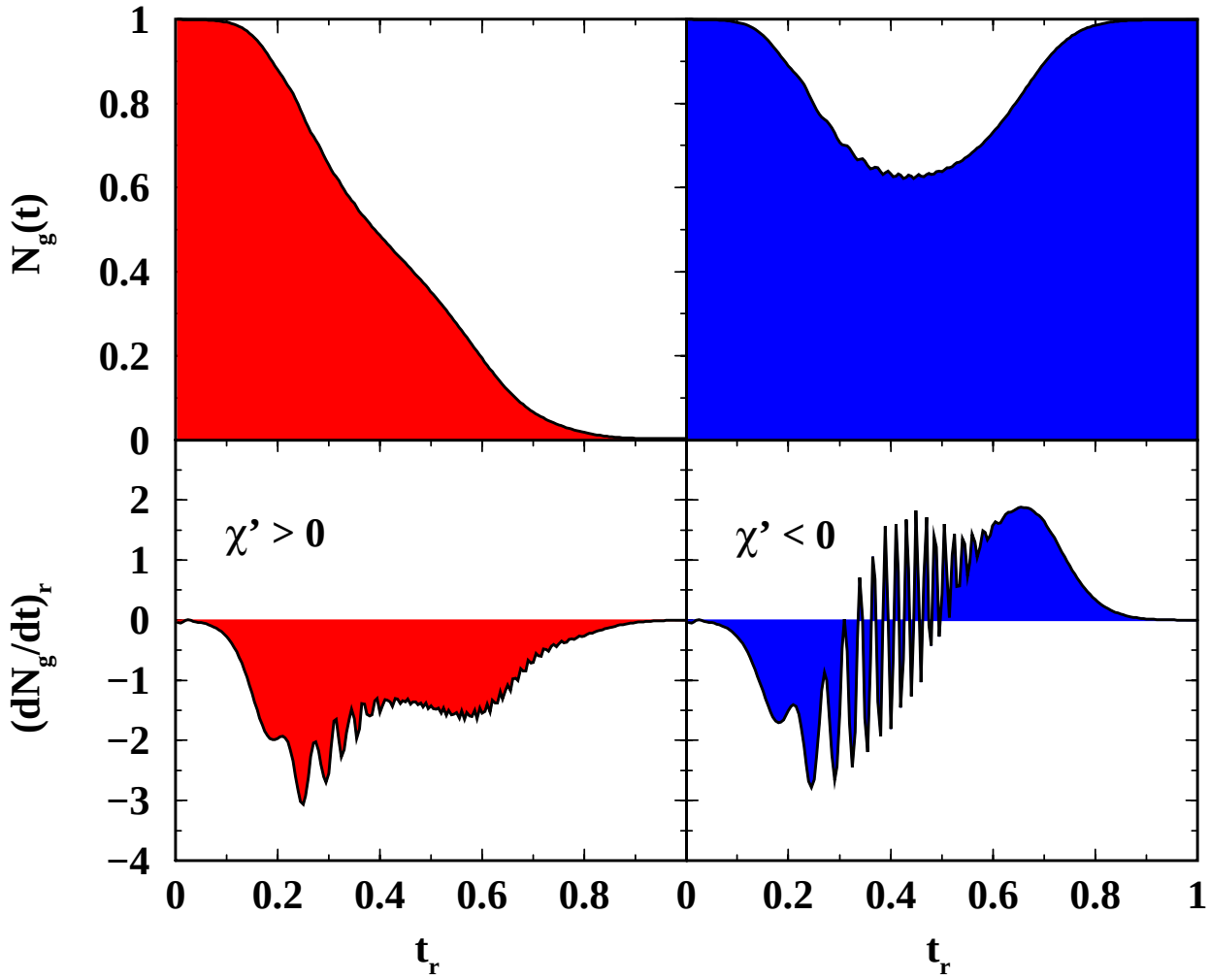

FIG. 3. Chirped field population transfer for $\chi' = 20$ in a two-potential system $V_g(r) = 0.$ and $V_e(r) = -2.r$. The positive chirp rate results in population inversion. The negative chirp rate leads to the break-out of population transfer efficiency. The relative quantities field parameters are defined in the Fig. 1, the intensity is stronger by the factor of five.

An extra feature in the two potential model (TPS) compared to the two level system (TLS) is the wavepacket dynamics on both the ground and excited electronic potentials. This dynamics induces an additional relative phase shift. If the dynamics is slow compared to the pulse duration this additional phase shift can be ommitted. This is the case in photoassociation of ultra cold atoms where the dynamics is slowed down[10]. Under these conditions the TPS is continuously approaching the TLS limit. Alternatively, the same effect

can be achieved in ultrafast spectroscopy where the pulse duration can be made shorter than the dynamics[7,11].

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